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Conversion of the Double Bonds of Dialkyl Maleates and Their Diels-Alder Adducts into γ -Butyrolactone Rings by Acetic Acid in Combination with Manganese (III) Acetate

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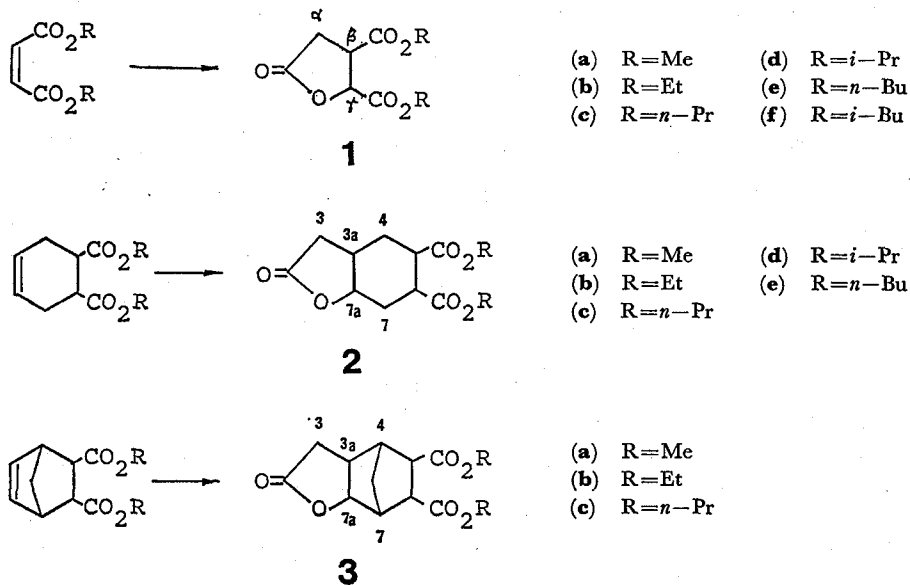
Reaction of each one of dialkylmaleates, 4-cyclohexene-1, 2-dicarboxylic acid dialkyl esters, and bicyclo [2.2.1] hept-5-ene-2, 3-dicarboxylic acid dialkyl esters with acetic acid in the presence of manganese (III) acetate dihydrate provided each one of β , γ -bis(alkoxycarbonyl)- γ -butyrolactones, 5, 6-bis(alkoxycarbonyl)-hexahydro-2(3H)-, and 5, 6-bis(alkoxycarbonyl)-hexahydro-4, 7-methano-2(3H)-*trans*-benzofuranones in moderate yields.

KEY WORDS: β , γ -Bis(alkoxycarbonyl)- γ -butyrolactones/ 5,6-Bis(alkoxycarbonyl)-hexahydro-2(3H)-*trans*-benzofuranones/ 5,6-Bis(alkoxycarbonyl)-hexahydro-4, 7-methano-2(3H)-*trans*-benzofuranones/

The best known reaction initiated by manganese(III) acetate is the free radical addition of carboxylic acids such as acetic,^{1,2)} propionic,²⁾ cyanoacetic,²⁾ malonic³⁾ and succinic²⁾ acids as well as malonamide⁴⁾ to the various olefins leading to a variety of γ -butyrolactones. The free radical addition of several aldehydes⁵⁾ and ketones⁶⁻⁸⁾ to olefins in the presence of manganese(III) acetate is also well known. In the former reaction, acyclic olefins without any distinction between internal and terminal as well as cyclic olefins have been used as the olefin component.^{2,9)} On the other hand, it has been reported²⁾ that, when alkyl acrylate was used as the olefin component, only very low yield (probably, negligible) of the corresponding lactone was obtained and that it may be attributed to the difficult oxidation of the adduct radical due to the presence of electron-withdrawing group in the α -position.

We now report that the reaction of dialkyl maleate (DAM) and their Diels-Alder adducts¹⁰⁾ with acetic acid in the presence of manganese(III) acetate dihydrate is easy process to occur if only a proper reaction conditions was applied. Especially, the success of reaction with DAM should be noted when considered with the difficult oxidation of intermediate adduct radical due to the presence of neighboring two alkoxycarbonyl groups.

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RESULT AND DISCUSSION

The obtained products, β,γ -bis(alkoxymethyl)- γ -butyrolactones(**1**), 5,6-bis(alkoxycarbonyl)-hexahydro-2(3H)-(**2**), and 5,6-bis(alkoxycarbonyl)-hexahydro-4, 7-methano-2(3H)-*trans*-benzofuranones(**3**), seem to be useful for the preparation of higher class of bridge-ring compounds and high polymers by utilizing the two alkoxycarbonyl groups as well as of hydroxy-containing tricarboxylic acids upon hydrolysis. As can be seen from Table I, the reasonable dilution of reaction mixture with acetic acid brings about the suppression of undesirable side-reactions such as chain transfer reaction of the intermediate adduct radical, although a longer reaction period is necessary (compare Run 1 or 2 to Run 4). In spite of the recovery of roughly same amount of the starting substrate in every runs, the yield of **1b** increased with increasing the amount of acetic acid used. The molar quantity of **1b** obtained in Run 4 is roughly near to that of consumed starting substrate, suggesting that, under the applied reaction conditions, the intermediate adduct radical has been oxidized into cationic species almost selectively though slowly. On the other hand, the use of acetic acid-acetic anhydride or acetic acid-potassium acetate mixture instead of acetic acid alone as the medium brought about a more rapid disappearance of manganese(III) acetate color, meaning a shorter reaction period, but the yield of **1b** has been greatly diminished. Thus, the favorable reaction conditions was applied to the free radical reaction of several dialkyl maleates with acetic acid providing the corresponding β,γ -bis (alkoxycarbonyl)- γ -butyrolactones (**1a** and **1c-f**). However, only the reaction period are somewhat differ from one another. As can be seen from Table III, the proton at C(β) of *cis*-**1** appears at approximately δ 3.4–3.8 as a multiplet, and the proton at C(γ) of *cis*-**1** appears at approximately δ 5.0–5.1 as a doublet. In case of *trans*-**1**, a multiplet (approximately δ 3.4–3.6) and a doublet (approximately δ 5.1–5.2) are

Conversion of Double Bonds into γ -Butyrolactone Rings

Table I. Conversion of Diethyl Maleate into β , γ -Bis (ethoxycarbonyl)- γ -butyrolactone (**1b**)

Run ^a	Molar ratio [Mn (OCOCH ₃) ₃ ·2H ₂ O/ Diethyl maleate]	CH ₃ CO ₂ H used	Reaction period (h) ^b	Yield of 1b ^c (%)	Recovered diethyl maleate ^c (%)
1	2	10 ml	5.0	18	49
2	3 ^d	20 ml	5.0	40	35
3	2	30 ml	5.0	53	35
4	2	40 ml	6.5	57	37
5	2	50 ml	7.0	56	42

- a) In every runs 2.0 mmol (0.344 g) of diethyl maleate was used.
b) The reaction mixture has been refluxed till the dark brown color of Mn(OCOCH₃)₃·2H₂O disappears.
c) Separated by column chromatography.
d) The employment of excess of Mn(OCOCH₃)₃·2H₂O, for example, such as 3 molar equivalents had no improvement in yield.

Table II. Conversion of DAM (other than Diethyl Maleate), CHD, and BHD into the Corresponding γ -Butyrolactone (**1a**, **1c-f**, **2**, and **3**)

Run ^a	Substrate	R	Reaction period (h) ^b	The γ -butyrolactone [and yield (%) ^c]	<i>cis/trans</i> ^d	Recovered substrate (%) ^e
1	DAM	Me	6.5	1a (44)	1/6.8	37
2	Diethyl fumarate ^e		7.0	1b (83)	1/5.7	19
3	DAM	<i>n</i> -Pr	7.0	1c (49)	1/4.2	31
4	DAM	<i>i</i> -Pr	6.5	1d (73)	1/4.2	17
5	DAM	<i>n</i> -Bu	7.0	1e (43)	1/3.9	43
6	DAM	<i>i</i> -Bu	7.0	1f (63)	1/4.2	26
7	CHD	Me	10.0	2a (51)	0	14
8	CHD	Et	8.0	2b (26)	0	52
9	CHD	<i>n</i> -Pr	9.0	2c (32)	0	52
10	CHD	<i>i</i> -Pr	9.0	2d (40)	0	56
11	CHD	<i>n</i> -Bu	8.0	2e (35)	0	62
12	BHD	Me	9.5	3a (42)	0	21
13	BHD	Et	9.5	3b (38)	0	19
14	BHD	<i>n</i> -Pr	9.0	3c (33)	0	19

- a) All runs were conducted by using 2.0 mmol of the substrate in 40 ml of CH₃CO₂H in the presence of 2 molar equivalents of Mn (OCOCH₃)₃·2H₂O.
b) After the reaction period under reflux, the color of Mn (OCOCH₃)₃·2H₂O disappeared.
c) Isolated by column chromatography.
d) Determined by ¹H-NMR spectra.
e) The reaction using diethyl fumarate was carried out in the same manner as others.

assigned to the proton at C(β) and that at C(γ), respectively. The *cis/trans* ratio of **1** was obtained from the integration of these signals. The oxidative addition of acetic acid to dialkyl maleates proceeded predominantly by *trans*-addition to their double bond. Probably, the internal rotation about C(1)-C(2) bond of cationic species, derived from oxydation of the intermediate adduct radical, brought about the most stable conformation of the cationic species. Thus, it is understandable that both the products derived from diethyl maleate and that from diethyl fumarate pos-

Table III. Physical Properties and Analytical Data of the Product

Compound	Mp (°C) or bp (°C/mmHg) ^{a)}	¹ H-NMR (δ , in CDCl ₃) ^{b)}		Found (Calcd) (%)	
		H-C(β) or H-C(γ) or [H-C (3a)]	[H-C (7a)]	C	H
1a	[131-136 (0.25)] [lit. ¹¹⁾ 149-154(1)] ^{c)}	<i>cis</i> -: 3.4-3.5 (m) <i>trans</i> -: 3.5-3.6 (m)	5.04 (d, J=8.4Hz) 5.10 (d, J=4.4Hz)	47.30 (47.53)	4.91 (4.99)
1b	[138-143 (0.25)]	<i>cis</i> -: 3.7-3.8 (m) <i>trans</i> -: 3.4-3.5 (m)	5.10 (d, J=8.4Hz) 5.15 (d, J=4.4Hz)	51.99 (52.17)	6.18 (6.13)
1c	[155-161 (0.25)]	<i>cis</i> -: 3.7-3.8 (m) <i>trans</i> -: 3.4-3.5 (m)	5.09 (d, J=8.4Hz) 5.15 (d, J=4.6Hz)	55.77 (55.80)	6.95 (7.03)
1d	[136-141 (0.25)]	<i>cis</i> -: 3.6-3.8 (m) <i>trans</i> -: 3.4-3.5 (m)	5.05 (d, J=8.4Hz) 5.10 (d, J=4.5Hz)	55.73 (55.80)	6.94 (7.03)
1e	[162-168 (0.25)]	<i>cis</i> -: 3.7-3.8 (m) <i>trans</i> -: 3.4-3.5 (m)	5.09 (d, J=8.4Hz) 5.14 (d, J=4.6Hz)	58.73 (58.73)	7.76 (7.75)
1f	[154-160 (0.25)]	<i>cis</i> -: 3.5-3.6 (m) <i>trans</i> -: 3.4-3.5 (m)	5.11 (d, J=8.4Hz) 5.17 (d, J=4.4Hz)	58.60 (58.73)	7.76 (7.75)
2a	[159-165 (0.28)]	[3.1-3.2 (m)]	[4.5-4.6 (m)]	56.18 (56.24)	6.11 (6.29)
2b	[164-170 (0.28)]	[3.2-3.3 (m)]	[4.6-4.7 (m)]	59.05 (59.14)	7.05 (7.09)
2c	[169-175 (0.28)]	[3.1-3.2 (m)]	[4.5-4.6 (m)]	61.43 (61.52)	7.39 (7.75)
2d	[159-165 (0.26)]	[3.1-3.2 (m)]	[4.5-4.6 (m)]	61.41 (61.52)	8.00 (7.75)
2e	[176-182 (0.30)]	[3.1-3.2 (m)]	[4.5-4.6 (m)]	63.29 (63.51)	8.22 (8.29)
3a	91-92 (Petroleum ether)	[3.1-3.2 (m)]	[4.88 (d, J=6.4Hz)] ^{d)}	58.43 (58.20)	5.87 (6.01)
3b	100-101 (Petroleum ether)	[3.0-3.1 (m)]	[4.78 (d, J=6.4Hz)] ^{d)}	60.71 (60.80)	6.69 (6.80)
3c	69-70 (Petroleum ether)	[3.1-3.2 (m)]	[4.84 (d, J=6.2Hz)] ^{d)}	62.88 (62.95)	7.42 (7.46)

a) Determined by bulb-to-bulb distillation.

b) Recorded on a 200 MHz instrument.

c) Obtained by ordinary distillation of pure *cis*-compound.

d) This signal seems not to be doublet of doublet.

sess an identical composition of *cis/trans* (see Run 2 of Table II); both products are symbolized with the same **1b**.

Further, we have used 4-cyclohexene-1,2-dicarboxylic acid dialkyl esters (CHD) and bicyclo[2.2.1] hept-5-ene-2,3-dicarboxylic acid dialkyl esters (BHD) instead of DAM as the starting substrate. The obtained products **2** have been found to have *trans*-configuration, because the proton at C(3a) and that of C(7a) appear at approximately δ 3.1-3.3 and δ 4.5-4.7 as only one multiplet, respectively. Analogous observation concerning the products **3** enabled us to determine that **3** possess only *trans*-configuration. This means that, in the cationic species in the course of reaction, the ring structure imposes restriction to rotation and that the nucleophilic attack of carboxymethyl oxygen occurs preferentially in such direction as that the thermodynamically more stable intermediate leading to *trans*-product, in which the γ -butyrolactone ring is fused to the cyclohexane ring in equatorial-equatorial relationship, is formed. The reaction conditions which has been applied for the reaction with CHD

or BHD seems not to be optimum. However, the yields of **2** or **3** were moderate when compared with those in cases using cycloaliphatic olefins such as cyclohexene.¹⁾

EXPERIMENTAL

Reaction of DAM, CHD, and BHD with Acetic Acid in the Presence of Manganese(III) Acetate Dihydrate. General Procedure: In a round-bottom flask equipped with a condenser were added the following: each one of DAM, CHD, and BHD (2.0 mmol), glacial acetic acid (40 ml), and manganese(III) acetate dihydrate (1.08 g, 4.0 mmol). The mixture was heated under reflux in a nitrogen atmosphere till the dark brown color of the manganese (III) acetate dihydrate disappears, after which the most part of acetic acid was removed under reduced pressure, and the mixture allowed to cool to room temperature. The resulting precipitate of manganese(II) acetate was separated by filtration and washed carefully with a small amount of ethyl acetate. The washing and filtrate were combined and evaporated under reduced pressure to afford a residue which was chromatographed on a silica gel column using 50% ethyl acetate-hexane as eluent.

Determination of the Optimum Amount of Acetic Acid in the Reaction with Diethyl Maleate. The reaction was conducted in a same manner as above with varying the amount of acetic acid used (see Table I).

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